Determination of reaction orders for the transesterification of canola oil with methanol by using KOH/MgO as a heterogeneous catalyst

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ARTICLE INFO

ABSTRACT

The reaction orders with respect to the reactants were determined for the reaction of canola oil with methanol catalyzed by KOH/MgO. The method of initial rates was used to determine the reaction rate. The experiments were carried out with different initial concentrations of methanol and canola oil. A very good correlation was found between the experimental and calculated reaction rates using the proposed equation. The reaction rate equations derived from Eley–Rideal and Langmuir–Hinshelwood mechanisms were discussed. As a result, the orders of reaction respect to both oil and methanol are concordant with the suggestion that the reaction takes place both homogeneously and heterogeneously.

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1. Introduction

Biodiesel is a clean and renewable alternative fuel which is also known as FAME (fatty-acid methyl ester) produced from both refined and waste vegetable oils and animal fats. TG (triglyceride) is the major component of vegetable oil and animal fats. Chemically, biodiesel is produced by transesterification of a TG with short chain alcohol like methanol in the presence of a catalyst. The reaction can be catalyzed homogeneously by sodium hydroxide and potassium hydroxide as base catalysts and by sulfuric acid as acid catalyst. The homogeneous base catalysts are the most commonly used since the reaction is faster and the reaction conditions are moderated [1]. However, the homogeneous base and acid catalysts are corrosive and process discharge large amount of waste water during removal of the catalysts from the reaction mixture [2]. The heterogeneous catalysts offer several advantages, such as they are noncorrosive, environmental friendly and not produce waste water.

The kinetics of biodiesel production homogeneous system has been investigated by research groups in several experimental studies [3–8]. Freedman et al. [3] studied the transesterification kinetics of soybean oil with 1-butanol. They observed the forward reaction was pseudo-first order and the reverse reaction was second order in the presence of excess alcohol. The kinetics of methanolysis of soybean oil using NaOH as catalyst was considered by Noureddin and Zhu [4]. In their study, where the kinetic model developed by Freedman et al. was used [3], they reported the second order kinetics for the three consecutive reactions [4,5]. Darnoko and Cheryan [6] studied the kinetics of methanolysis of palm oil using KOH as catalyst. They stated the second order kinetics for first 30 min of the reaction and first order kinetics for the rest of the reaction. Vicente et al. [7] proposed a kinetic model for transesterification of sunflower oil with methanol in the presence of KOH catalyst. Their reaction mechanism model includes initial mass transfer controlled region and then followed by kinetically controlled region. The mass transfer controlled regime was neglected at a stirring rate of 600 rpm. Also, they found that the kinetically controlled regime followed a second order kinetics for the forward and reverse reactions. In another study by Vicente et al. [8] same kinetic model was proposed for methanolysis of *Brassica carinata* oil using KOH as a catalyst.

The kinetics of heterogeneously catalyzed biodiesel production was sparsely studied in the literature. Singh and Fernando [9] researched the kinetics of transesterification of soybean oil with methanol using PbO, MnO$_2$, BaO, CaO and MgO heterogeneous catalysts. They performed experiments under high pressure and high temperature conditions. They reported the overall reaction orders were found to be 1 for PbO, MnO$_2$, CaO and MgO catalysts. The kinetics of sunflower oil with methanol was investigated using CaO by Veljkovic et al. [10] and using Ca(OH)$_2$ by Stamenkovic et al. [11]. It has been reported the overall reaction followed the pseudo-first order reaction kinetics in these studies [10,11].

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Nomenclature

C_{TG} concentration of TG (mole/l)
C_M concentration of M (mole/l)
C_{TG0} initial concentration of TG (mole/l)
C_{M0} initial concentration of M (mole/l)
DG diglyceride
E ester
FAME fatty-acid methyl ester
G glycerin
k rate constant $(l^{\alpha+\beta}/mole^{\alpha+\beta-1})(g^{-1} cat\ min^{-1})$
K_A adsorption constant of methanol, $(kA/k-A)(l/mole)$
K_{A2} adsorption constant of triglyceride, $(kA2/k-A2)$ (l/mole)
M methanol
MG monoglyceride
N_{TG} mole amount of TG (mole)
N_{TG0} initial mole amount of TG (mole)
r_{TG} reaction rate of TG (mole/g cat × min)
r_{TG0} initial reaction rate of TG (mole/g cat × min)
S catalytic surface
TG triglyceride
W catalyst amount (g)
X_{TG} conversion of TG
Y_F FAME yield
α reaction order of TG
β reaction order of M

The aim of this study is to determine the reaction orders of with respect to the reactants for transesterification of canola oil with methanol using 20 wt.% KOH/MgO heterogeneous catalyst. The method of initial rates was used to define the reaction rate. In order to explain the Power Law rate model expression the reaction rate equations derived from Eley–Rideal and Langmuir–Hinshelwood mechanisms were discussed.

2. Kinetic model

The overall transesterification reaction of triglycerides with methanol can be represented as the following equation:

$$TG + 3M \overset{catalyst}{\rightleftarrows} 3F + G \tag{1}$$

where TG is triglyceride, M is methanol, F is FAME, and G is glycerin. In a batch reactor, the differential form of the design equation for a heterogeneous reaction is:

$$-r_{TG} = -\frac{1}{W}\frac{dN_{TG}}{dt} = \frac{N_{TG0}}{W}\cdot\frac{dX_{TG}}{dt} \tag{2}$$

where r_{TG} is the reaction rate of TG, dN_{TG}/dt is the consumption of TG per unit time, W is catalyst amount, N_{TG0} is the initial mole amount of TG, and dX_{TG}/dt is the conversion of TG per unit time. The reaction can be considered as irreversible when the FAME concentration is significantly lower than methanol concentration. The reaction can also be accepted to be irreversible due to the excess amount of methanol in the reaction. According to Power Law model the irreversible rate equation can be written as:

$$-r_{TG} = kC_{TG}^{\alpha}C_M^{\beta} \tag{3}$$

where k is the rate constant, α is reaction order of TG, β is reaction order of M, C_{TG} and C_M are concentrations of the reactants

TG and M, respectively. Therefore from Eqs. (2) and (3), Eq. (4) can be expressed as:

$$-r_{TG} = \frac{N_{TG0}}{W}\cdot\frac{dX_{TG}}{dt} = kC_{TG}^{\alpha}C_M^{\beta} \tag{4}$$

The method of initial rates might be applied to determine the reaction orders α and β. If Eq. (4) is written in terms of initial rate of TG (r_{TG0}), Eq. (5) is obtained.

$$-r_{TG0} = \left(\frac{N_{TG0}}{W}\cdot\frac{dX_{TG}}{dt}\right)_0 = kC_{TG0}^{\alpha}C_{M0}^{\beta} \tag{5}$$

where C_{TG0} and C_{M0} are initial concentration of the reactants TG and M. The following equation is obtained by taking the natural logarithm of Eq. (5):

$$\ln\left(\frac{N_{TG0}}{W}\cdot\frac{dX_{TG}}{dt}\right)_0 = \ln k + \alpha \ln C_{TG0} + \beta \ln C_{M0} \tag{6}$$

Let $Y = \ln(N_{TG0}/W)(dX_{TG}/dt)_0$, $a_0 = \ln k$, $a_1 = \alpha$, $X_1 = \ln C_{TG0}$, $a_2 = \beta$ and $X_2 = \ln C_{M0}$. Eq. (6) can be expressed as:

$$Y = a_0 + a_1 X_1 + a_2 X_2 \tag{7}$$

If N experimental runs carry out for the jth run, then Eq. (7) takes the form:

$$Y_j = a_0 + a_1 X_{1j} + a_2 X_{2j} \tag{8}$$

a_0, a_1 and a_2 parameters for Eq. (8) are found by solving Eq. (9) through (11) simultaneously using least squares method. For N runs, 1, 2, ..., N,

$$\sum_{j=1}^{N} Y_j = Na_0 + a_1\sum_{j=1}^{N} X_{1j} + a_2\sum_{j=1}^{N} X_{2j} \tag{9}$$

$$\sum_{j=1}^{N} X_{1j}Y_j = a_0\sum_{j=1}^{N} X_{1j}a_1\sum_{j=1}^{N} X_{1j}^2 + a_2\sum_{j=1}^{N} X_{1j}X_{2j} \tag{10}$$

$$\sum_{j=1}^{N} X_{2j}Y_j = a_0\sum_{j=1}^{N} X_{2j} + a_1\sum_{j=1}^{N} X_{1j}X_{2j} + a_2\sum_{j=1}^{N} X_{2j}^2 \tag{11}$$

3. Materials and methods

The 20 wt.% KOH/MgO catalyst was prepared by incipient wetness impregnation method. An aqueous solution of KOH (Merck, 105012) was loaded on magnesia (Merck, 105862). The catalyst was dried at 393 K for 16 h and calcined at 773 K for 5 h. The characterization and preparation of catalyst were presented in our previous study [12]. The food grade canola oil, whose free fatty acid and water contents were less than 1%, was obtained from local market. A 250 ml 3-necked glass flask fitted with condenser was charged with 50 g of canola oil and different volumes of methanol. Reactions were performed at stirring rate of 1000 rpm 3 wt.% of catalyst based on the oil, and at methanol reflux temperature. After the reaction temperature was reached to reflux temperature of methanol, catalyst was added to reaction mixture and reaction time was set as zero. Samples were taken from the reaction medium at 1 min intervals to 5 min and analyzed separately. The samples were separated from catalyst and glycerol by spinning in a centrifuge at 5000 rpm for 10 min. The excess methanol was removed from the sample by evaporation. Finally, the FAME yield was determined using gas chromatograph (Agilent 6890 GC with a HP INNOwax capillary column) according to EN 14103. Methyl heptadecanoate solution (10 mg/mL) was used as internal standard. Details of analysis conditions were given in our previous study [12]. All analyses were repeated three times and average values considered.

Table 1
Effect of methanol to oil (TG) initial mole ratio on FAME yield.

t (min)	M/TG initial mole ratio					
	9/1		12/1		15/1	
	FAME (%)	X_{TG}	FAME (%)	X_{TG}	FAME (%)	X_{TG}
0	0	0	0	0	0	0
1	1.70	0.0170	0.74	0.0074	1.99	0.0199
2	4.69	0.0469	4.96	0.0496	4.14	0.0414
3	8.03	0.0803	5.46	0.0546	5.50	0.0550
4	9.48	0.0948	9.48	0.0948	8.86	0.0886
5	10.76	0.1076	11.96	0.1196	11.18	0.1118

4. Results and discussion

4.1. Mass transfer analysis

Introductory experiments were carried out with different stirring speeds in order to determine the influence of external mass transfer on the reaction rate. The influence of stirring speed on FAME yield was performed in the range of 250–1000 rpm while the other reaction parameters were kept constant, such as; methanol to oil molar ratio, 6:1; temperature, reflux temperature; catalyst amount, 3 wt.%; reaction time, 9 h. These reaction conditions were chosen according to our previous study [12], since the highest FAME yield of 95.05% was obtained at these conditions. The FAME yields of about 95% were achieved in all experiments done with changing stirring speed. These results suggest that interparticle diffusion is unimportant and does not control the reaction rate. Hence, all kinetic experiments were performed at a stirring rate of 1000 rpm. This observation was also confirmed in literature [7,13].

In slurry reactors, intraparticle heat transport limitations are generally negligible due to the relatively small particle sizes (<125 μm). As a result of small catalyst particle size, mass and heat transfer limitations between the catalyst and reactants were considered negligible in this study.

4.2. Determination of the reaction kinetics

Kinetic experiments were implemented with different initial concentrations of M and TG at three different methanol to oil ratios in order to find reaction orders α and β. The obtained results are given in Table 1.

The conversion of TG (X_{TG}) and FAME yield (Y_F) is equal to each other according to the Eqs. (12)–(14)

$$C_{TG} = C_{TG0}(1 - X_{TG}) \quad (12)$$

$$Y_F = \frac{1}{3}\frac{C_F}{C_{TG0}} \quad (13)$$

$$C_{TG} = C_{TG0} - \frac{1}{3}C_F \quad (14)$$

By substituting Eq. (13) into Eq. (14), Eq. (12) can be transformed to give Eq. (15):

$$C_{TG} = C_{TG0}(1 - Y_F) \quad (15)$$

According to Eqs. (12) and (15), the X_{TG} is equal to Y_F. The results shown in Figs. 1–3 indicate that X_{TG} values are linear with reaction time. Thus, the initial reaction rate value ($-r_{TG0}$) for each experiment can be determined by multiplying the slope (dX_{TG}/dt) by N_{TG0}/W. The initial reaction parameters and obtained initial reaction rates are tabulated in Table 2.

Table 3 is constructed by using the values in Table 2. The following equations were obtained by substituting the appropriate values from Table 3 into Eq. (9) through (11):
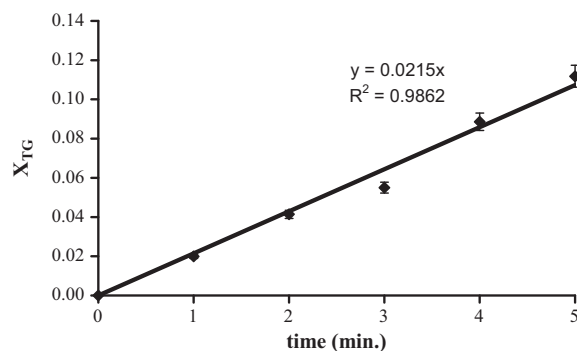
$$-18.8718 = 3a_0 - a_1 0.6055 + a_2 6.7849 \quad (16)$$
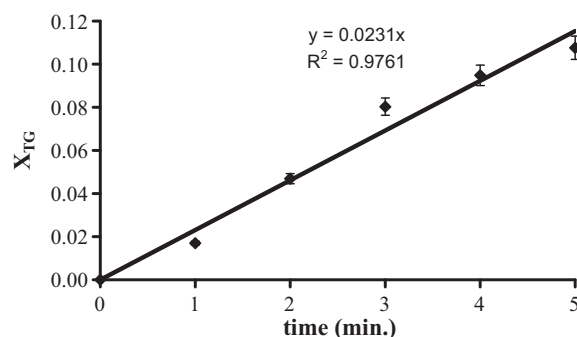
Fig. 1. TG conversion (X_{TG}) at 9/1 molar ratio as a function of reaction time.
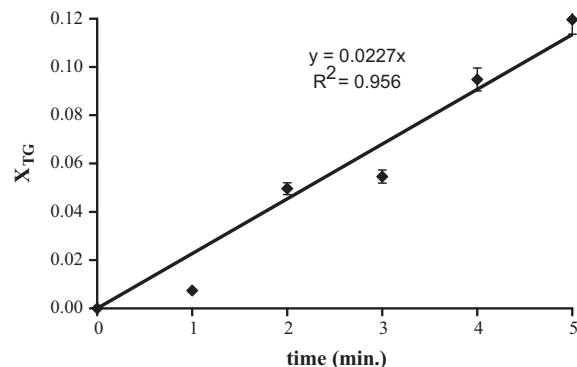
Fig. 2. TG conversion (X_{TG}) at 12/1 molar ratio as a function of reaction time.

Fig. 3. TG conversion (X_{TG}) at 15/1 molar ratio as a function of reaction time.

$$3.8160 = -a_0 0.6055 + a_1 0.1420 - a_2 1.4005 \quad (17)$$

$$-42.6920 = a_0 6.7849 - a_1 1.4005 + a_2 15.3941 \quad (18)$$

a_0, a_1 and a_2 parameters were computed by solving Eq. (16) through (18) simultaneously. Recalling that $a_0 = \ln k$, $a_1 = \alpha$ and $a_2 = \beta$, the reaction rate constant (k) was calculated as 8.1622×10^{-4} ($l^{\alpha+\beta}$/mole$^{\alpha+\beta-1}$)(g^{-1} cat min^{-1}) and the reaction orders were calculated to be $\alpha = 1.08$ and $\beta = 0.46$. So, the general rate equation was written as:

$$-r_{TG0} = 8.1622 \times 10^{-4}C^{1.08}C^{0.46} \quad (19)$$

The experimental initial reaction rate and calculated initial reaction rate values were plotted using Eq. (19) (see Fig. 4). A very good correlation was found between the experimental and calculated initial reaction rates. The proposed kinetic model fits very well with our experimental observations.

Biodiesel synthesis with homogeneous catalysts such as sodium hydroxide and potassium hydroxide proceeds by the formation of methoxide anions. Generally, any heterogeneously catalyzed

Table 2
Initial reaction parameters and obtained initial reaction rates.

M/TG initial mole ratio (mole/mole)	W (g)	N_{TG0} (mole)	N_{M0} (mole)	C_{TG0} (M)	C_{M0} (M)	$(-r_{TG})_0$ (mole/g cat × min)
9:1	1.5	0.124	1.116	0.9041	8.1376	0.001910
12:1	1.5	0.124	1.488	0.8146	9.7753	0.001877
15:1	1.5	0.124	1.860	0.7411	11.1177	0.001777

Table 3
Data for linearized least-squares analysis.

	$X_1 = \ln C_{TG0}$	$X_2 = \ln C_{M0}$	$Y = \ln(-r_{TG0})$	$X_1 Y$	X_1^2	$X_1 X_2$	$X_2 Y$	X_2^2
	−0.1008	2.0965	−6.2609	0.6312	0.0102	−0.2114	−13.1259	4.3953
	−0.2051	2.2799	−6.2783	1.2874	0.0420	−0.4675	−14.3137	5.1978
	−0.2996	2.4085	−6.3326	1.8974	0.0898	−0.7216	−15.2524	5.8011
Sum	−0.6055	6.7849	−18.8718	3.8160	0.1420	−1.4005	−42.6920	15.3941
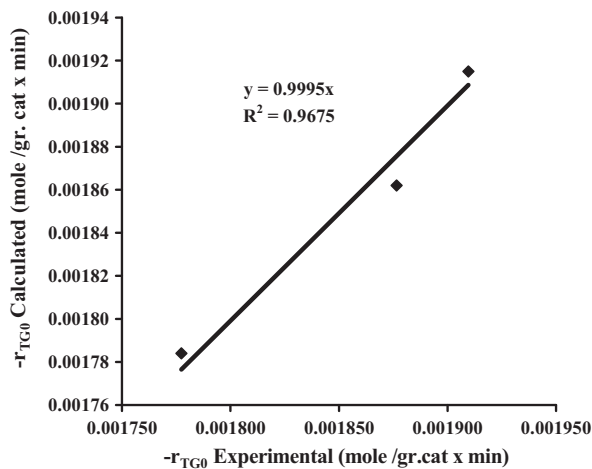
Fig. 4. Experimental versus calculated initial reaction rates.
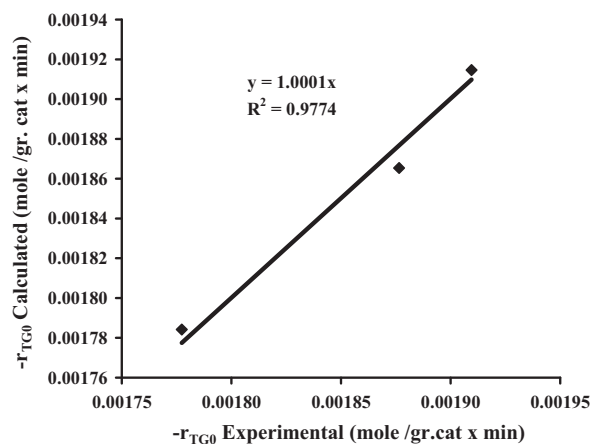
Fig. 5. Experimental versus calculated initial reaction rates based on Eley–Rideal mechanism where the surface reaction is assumed to be the rate limiting step.

reaction involves the adsorption, surface reaction and desorption steps. In literature, methanol adsorption step was assumed as a rate determining step for heterogeneously catalyzed biodiesel synthesis [14–16]. Dossin et al. [16] proposed the Eley–Rideal type kinetic model for the transesterification of ethyl acetate with methanol in presence of MgO as a heterogeneous catalyst, where methanol adsorption was assumed as the rate determining step. Their model was based on the reaction between adsorbed methanol on the MgO surface and ethyl acetate from the liquid phase.

In this study, the reaction orders respect to the TG and M were determined by measuring the initial reaction rates using different initial concentrations of the reactants. The reaction orders were calculated as 1.08 for TG and 0.46 for M. Kinetic equation for the heterogeneously catalyzed reactions can be written as [17]:

$$\text{rate} = \left(\frac{\text{kinetic factor\_driving} - \text{force group}}{\text{adsorption group}} \right) \quad (20)$$

Table 4 shows the mechanisms and rate equations which are derived from the Eley–Rideal mechanism and Langmuir–Hinshelwood mechanism. The Eley–Rideal type mechanism where the methanol adsorption is assigned to be the rate determining step, the initial rate equation consists of only methanol concentration that means the rate equation is independent from TG concentration. In the Langmuir–Hinshelwood type mechanism where the methanol adsorption is assumed as the rate determining step, the initial rate equation contains TG concentration term in denominator. It means that TG is adsorbed although the methanol adsorption is the rate determining step. These rate equations are in contradiction with our experimental

results. In the Eley–Rideal type mechanism where the surface reaction is assumed to be the rate determining step, the methanol concentration term appears both nominator and denominator of the initial rate equation. The appearance of TG and methanol terms in nominator indicates that both reactants act as a driving force for the reaction. In the rate determining step (surface reaction) TG reacted with adsorbed methanol, so the rate equation contains methanol concentration term in its denominator which indicates methanol adsorption. According to Eley–Rideal mechanism where the surface reaction is assumed to be the rate limiting step, it is expected that the appearance of TG concentration term in nominator and reaction order of TG (α) is positive. Since the catalyst dissolved in reaction medium, the reaction proceeds both heterogeneously and homogeneously. So, as it is expected the order of TG (α) is close to 1 according to rate equations of both homogeneous and heterogeneous reaction. The decrease of the reaction order of methanol (β) is explained by the appearance of methanol concentration in denominator in heterogeneous rate equation. The homogeneous reaction rate effect tends to increase reaction order of methanol (β) while the heterogeneous reaction rate effect has a tendency to decrease.

The calculated reaction rate constants and adsorption constants for Eley–Rideal and Langmuir–Hinshelwood mechanisms are also represented in Table 4. The constants of initial rate equations were solved using nonlinear regression method using MATLAB 7.0. The negative value for K_A and k can be ruled out because the adsorption constant and the rate constant cannot be negative. These results support the validity of Eley–Rideal mechanism where the surface reaction is assumed to be the rate limiting step. If the experimental

Table 4
Proposed Hougen–Watson reaction mechanisms.

Mechanism	Limiting rate and rate equation	Initial rate equation and calculated constants
Eley–Rideal	Methanol adsorption $$-r^1 = \frac{k(C_M - C_{DG}C_E K/C_{TG}}{1 + C_{DG}C_E K/C_{TG} + C_E K_D}$$	$-r_0^1 = KC_{M0}$ $k = -4 \times 10^{-5}$ (l/g cat × min)
$M + S \Leftrightarrow M \cdot S$ $TG + M \cdot S \Leftrightarrow DG + E \cdot S$ $DG + M \cdot S \Leftrightarrow MG + E \cdot S$ $MG + M \cdot S \Leftrightarrow G + E \cdot S$ $E \cdot S \Leftrightarrow E + S$	Surface reaction $$-r^1 = \frac{k(C_{TG}C_M K_A - C_{DG}C_E K)}{1 + C_M K_A + C_E K_D}$$	$-r_0^1 = \frac{kC_{TG0}C_{M0}}{1 + C_{M0}K_A}$ $k = 5.794 \times 10^{-4}$ (l²/mole × g cat × min) $K_A = 0.15072$ l/mole
Langmuir–Hinshelwood	Methanol adsorption	$-r_0^1 = \frac{kC_{M0}}{1 + C_{TG0}K_{A2}}$ $k = 6.6561 \times 10^{-5}$ (l/g cat × min)
$M + S \Leftrightarrow M \cdot S$ $TG + S \Leftrightarrow TG \cdot S$ $TG \cdot S + M \cdot S \Leftrightarrow DG + S + E \cdot S$ $DG + M \cdot S \Leftrightarrow MG + S + E \cdot S$ $MG + M \cdot S \Leftrightarrow G + S + E \cdot S$ $E \cdot S \Leftrightarrow E + S$	$$-r^1 = \frac{k(C_M - C_{DG}C_E K/C_{TG})}{1 + C_{DG}C_E K/C_{TG} + C_{TG}K_{A2} + C_E K_D}$$	$K_{A2} = -0.79431$ (l/mole)
Homogeneous reaction $TG + 3M \Leftrightarrow 3F + G$	$-r^1 = kC_{TG}C_M^3 - k_{-1}C_G C_F^3$	$-r_0^1 = kC_{TG0}C_{M0}^3$

TG, triglyceride; M, methanol; DG, diglyceride; MG, monoglyceride; G, glycerine; E, ester; S, catalytic surface; K_A, adsorption constant of methanol ($=kA/k - A$) (l/mole); K_{A2}, adsorption constant of triglyceride ($=kA2/k - A2$) (l/mole); k reaction rate constant.

and calculated reaction rate values were plotted (see Fig. 5), a very good correlation was found between the experimental and calculated reaction rates. It is concordant with the obtained Power Law rate equation and also fits very well with our experimental observations.

5. Conclusions

In this study, we investigated the reaction orders of TG and methanol as presented in Eq. (3) in the presence of KOH/MgO as a heterogeneous catalyst. The method of initial rates was applied to determine the reaction orders and rate constant. The reaction order of TG (α) was experimentally found to be 1.08. The reaction order of methanol (β) was experimentally found to be 0.46. The order of methanol (β) is 3 according to homogeneous reaction rate equation. The reaction order of 0.46 with respect to methanol (β) was assessed as concordant with the reaction proceeds both homogeneously and heterogeneously. The reaction rate equations derived from Eley–Rideal and Langmuir–Hinshelwood mechanisms were used to explain the Power Law rate model expression. The obtained results support the validity of Eley–Rideal mechanism where the surface reaction is assumed to be the rate limiting step.

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